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Russian Article

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CORROSION OF METALLIC MATERIALS IN AQUEOUS SOLUTIONS OF FLUORIDES AT HIGH TEMPERATURES

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The considerable aggressiveness of solutions of hydrofluoric acid with respect to most metallic materials is well known. In moist fluoride salts, especially in bifluorides and their aqueous solutions, where the free acid is present, considerable corrosion of metals occurs.

We have found only several studies in the literature, pertaining to an investigation of the corrosion resistance of various materials in solutions of fluorides and bifluorides [1, 2]. A large number of studies has been devoted to the corrosion of materials in aqueous solutions of HF [3-10].

The corrosion resistance of metals in hydrogen fluoride and its salts depends to a considerable degree on the composition of the films, i.e., on the composition of the solid phase that is formed as a result of corrosion at the metal surface.

For testing samples of metallic materials in aqueous solutions of fluorides of different temperatures, we used test tubes made of fluoroplast-4 [teflon] (50 ml capacity), with screw caps of the same material. Samples of the metals were placed in these test tubes, and a solution of fluoride was poured in. The test tubes were placed in an incubator, where they were kept at the desired temperature correct to $\pm$ 0.5°C.

In tests of materials in solutions of ammonium fluoride at temperatures above 80°C, ammonium bifluoride is formed, and the salt undergoes thermal dissociation [11] into NH_3 and HF, as a result of which a slight pressure was created in the hermetic test tubes during their heating.

The Table shows the corrosion resistance of metals in solutions of fluorides and bifluorides at different temperatures. For comparison the right-hand corner of the Table presents the corrosion rates of the same metals in hydrofluoric acid.

The data obtained show that fluoride solutions are less aggressive than hydrofluoric acid with respect to iron-base alloys. Noteworthy is the high stability of steel EI-533 (1Kh23N23M3D3), both in hot solutions of fluoride, and in hydrofluoric acid.

Aluminum and its alloys are greatly decomposed in solutions of bifluorides, and especially in hydrofluoric acid. They can be used in neutral salt solutions. In hydrofluoric acid the corrosion resistance of copper and its alloys depends on the presence of oxygen of the air.

In hot solutions of fluorides and hydrofluoric acid, copper is less stable than its alloys. In these solutions, brass and bronze are subject to corrosion cracking, with the deposition of a spongy copper precipitate on the surface. Monel metal and nickel are the stablest materials in hot solutions of fluorides and hydrofluoric acid. Lead is suitable for hot solutions of NH_4F and $NH_4F \cdot HF$ and cold solutions of HF.

The data given enable us to recommend a material for the construction of heat exchangers operating in fluorides, depending on their properties and the temperature.

Corrosion Rates of Metallic Materials in Aqueous Solutions of Fluorides and in Hydrofluoric Acid, $g\text{-}m^2/hr$
Duration of Tests 670 hrs (A -- in solution; B -- in vapors)

Material	Potassium bifluoride, AMG-3						Ammonium fluoride							
	50% p-p, 50°		50%p-p, 100°		90%p-p, 115°		50%p-p, 50°		50%p-p, 70°		50%p-p, 90°		80%p-p, 115°	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Steel Z	0.0035	0.01	-	-	-	-	0.11	0.065	-	-	-		-	-
Steel 12Kh5MA	-	-	-	-	-	-	0.045	0.066*	-	-	-	-	-	-
Steel 30KhGSA	-	-	-	-	-	-	0.88	0.076*	-	-	-	-	-	-
Steel 1Kh13	-	-	-	-	-	-	0.20	0.19	-	-	-	-	-	-
1Kh18N9T	0.018	0.011	-	-	-	-	0.026	0.030	0.04	0.05	0.27	0.12	0.13*	0.026*
1Kh18N12MZT	0.003	0.013	-	-	-	-	-	-	-	-	0.24	0.1	0.035	0.052**
1Kh23N23M3D3	0.002	0.004	0.03	0.06	0.003	0.003	-	-	0.010	0.018	0.013	0.08	0.135	0.016
Aluminum AD-1	weight gain 0.03	0.001	0.145	0.27*	0.34	0.07*	0.015	0.012	0.005	0.005	0.012	0.001	0.18	0.062
Alloy AMTs	weight gain 0.045	0.040	-	-	-	-	-	-	-	-	-	-	-	-
Alloy AMG-Z	-	-	-	-	-	-	0.007	0.007	-	-	-	-	-	-
Duralumin D16	-	-	-	-	-	-	0.020	0.018	-	-	-	-	-	-
Magnesium MG-1	0.008	-	-	0.05**	0.004	0.01	-	-	0.14	0.14	0.41	0.037	0.95	0.025**
Titanium VT-1	0.003	0.002	-	-	-	-	0.04	0.035	-	-	-	-	-	-
Copper M-2	0.009	0.0145	0.018	0.0090	0.010	0.006	0.62	1.90*	-	-	-	-	-	-
Brass LS-59-1	-	-	-	-	-	-	0.60	1.35	-	-	-	-	-	-
Bronze A5	-	-	-	-	0.003***	0.009***	-	-	-	-	-	-	-	-
Bronze AN	-	-	-	-	0.038***	0.014***	-	-	-	-				
Monel metal	0.17	0.067	0.013	0.0500	0.004	0.002	-	-	-	-	0.067	0.026	0.026	0.015
Nickel N-2	0.029	0.012	0.021	0.002	-	-	-	-	0.01	0.05	0.015	0.010	0.047	0.020
Lead S-2	0.125*	0.295	0.19	0.76	0.12	0.16	-	-	0.06	0.28	0.09	0.35	0.26	0.17

Note. The character of the corrosion was uniform, except for: * point corrosion; ** pitting corrosion; *** deposition of spongy copper precipitate on the surface; **** stress corrosion cracking.

p-p = Solution.

[Table continued]

Material	Ammonium bifluoride				Hydrofluoric acid			
	50% p-p, 50°		80% p-p, 90°		80% p-p, 115°		40% 20°	40% 108-112°
	A	B	A	B	A	B		On the vapor-liquid boundary
Steel Z	0.82	0.75	4.79	5.56	4.8	5.5	5.5	70
Steel 12Kh5MA	-	-	-	-	-	-		
Steel 30KhGSA	-	-	-	-	-	-		
Steel 1Kh13	-	-	-	-	-	-	6.5	
1Kh18N9T	0.81	0.28	0.86**	0.96**	0.09	0.2	4.5	
1Kh18N12MZT	-	0.16**	0.12	0.33**	0.07	0.22**		48.0
1Kh23N23M3D3	-	0.04	0.08	0.13	0.086	0.10		0.5
Aluminum AD-1	0.63	0.63	0.94**	0.87**	Dissolved completely		highly soluble	highly soluble
Alloy AMTs	0.45*	0.27*	-	-	-	-		
Alloy AMG-Z	-	-	-	-	-	-		
Duralumin D-16	-	-	-	-	-	-		
Magnesium MG-1	-	-	0.11	0.28**	1.57**	1.54**		
Titanium VT-1	3.8	2.65	-	-	-	-	highly soluble	highly soluble
Copper M-2	0.04	0.10	-	-	-	-		0.05
								In absence of oxygen 1.2***
								In presence of 0.02% oxygen
Brass LS-59-1	-	-	-	-	-	-	1.26****	1.1****
Bronze A5	-	-	-	-	-	-		0.25****
Bronze AN	-	-	-	-	-	-		0.22****
Monel metal	0.038	0.031	0.03	0.11	0.02	0.09	0.05	0.05
								In absence of oxygen
Nickel N-2	0.05	0.075	0.02	0.08	0.13	0.06	0.2	0.5
Lead S-2	0.15	0.20	0.14	0.13	0.11	0.23	0.25	4.6

Note: p-p = Solution

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